Trivalent Chromium Electroplating
For Baths Containing Hypophosphite Ions
By Jin-Yih Hwang

The effects of composition and operating conditions on deposits and current efficiencies were investigated in many different trivalent chromium plating processes containing hypophosphite ions. The surface morphology of the deposits was observed by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy.

Conventional hexavalent chromium electroplating baths deposit the metal at low cathode efficiency and have poor covering and throwing power. The processes also generate hazardous wastes. To overcome many of the disadvantages of hexavalent chromium plating, the use of trivalent chromium has been advocated. In 1950, Yoshida first studied trivalent chromium plating, using ammonium sulfate and urea. Ishaguro reported the use of chromium sulfamate and urea. Since then, many others have worked in this field to reach the current level of development. In the decade just past there are numerous reports describing the trivalent chromium electroplating process using completing agents such as malic acid, sodium thiocyanate, aspartic acid, glycine, glycolic acid, and formate. This study investigated trivalent chromium plating electrolyte solutions containing hypophosphite ions as a completing agent.

Experimental Procedure
The prepared plating solutions contained trivalent chromium, hypophosphite (H$_2$PO$_2^-$), ammonium ions, and boric acid. The pH of the solutions could be adjusted with sulfuric acid, hydrochloric acid and sodium hydroxide. The Hull cell used consisted of two electrodes. The anode was made of platinized titanium, 5 x 5 cm graphite sheets, lead alloys and carbon fibers. The cathode was made of copper sheets and stainless steel (5 x 10 cm). Pretreatment of the cathode consisted of decreasing in trichloroethylene, water rinsing, dipping in acid, and water rinsing. Metal concentration of the solutions was analyzed quantitatively by atomic absorption spectrometry.

The current efficiency ($\eta$) of chromium is determined by

$$\eta = \frac{\Delta C}{V \cdot t \cdot F}$$

where $V$ is the volume of the plating bath in liters, $\Delta C$ is the change in molar concentration of chromium after electrolysis (moles/liter), $t$ is the constant current through the cell (A), $F$ is Faraday's Constant (96,486 coulombs/equivalent).

Shimadzu Model 245
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The surface morphology and structure of the deposits were observed by SEM and characterized by X-ray diffractometry.

Results and Discussion
The eight sources used for trivalent chromium were KCr(SO$_4$)$_2$·12H$_2$O, Cr(ClO$_4$)$_3$, Cr(NO$_3$)$_3$, Cr(CH$_3$COO)$_3$, Cr(NH$_2$SO$_3$)$_3$, Cr(SCN)$_3$, Cr$_2$(SO$_4$)$_3$·10H$_2$O, and CrCl$_3$·6H$_2$O. These compounds were dissolved respectively in aqueous solutions containing 2.2M NaH$_2$PO$_2$, 3.2M NH$_4$Cl, 0.2M H$_3$BO$_3$ and 0.1M NaF to prepare 0.2M trivalent chromium solutions. The solutions were electrolyzed in Hull cells at 7.5 A to obtain chromium deposits. All the chromium compounds produced colored deposits except Cr$_2$(SO$_4$)$_3$·10H$_2$O, Cr(ClO$_4$)$_3$, and CrCl$_3$·6H$_2$O. These three produced bright white, attractive deposits, though not exactly the same as the blue white of conventional hexavalent chromium deposits. Considering the volatility, conductivity, cost and color of deposits, the optimal trivalent salts are chromic chloride and chromic sulfate.

![Fig. 1 — Effect of trivalent chromium concentration on current efficiency (percent) for trivalent chromium hypophosphite plating baths.](image)

**Effect of Concentration**
Solutions of chromic chloride containing 2.2M NaH$_2$PO$_2$, 3.2M NH$_4$Cl, 0.2M H$_3$BO$_3$, and 0.1M NaF were prepared in the following concentrations: 0.01, 0.02, 0.03, 0.05, 0.06, 0.073, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.8 M and placed in Hull cells. They were then electrolyzed for three and six minutes at an average current density of 0.15 A/cm$^2$. Temperature was maintained in the range of 23 to 42 °C. It was found that the electrode voltage drops were 7.7 to 8.0 volts during the experiments. Figure 1 shows that upon increasing the concentration of trivalent chromium, current efficiencies are first increased, then slightly decreased for concentrations in the range of 0.01 to 0.5 M.
The SEM photographs of Fig. 2 show deposits having nodular surfaces, possibly caused by high current density. Fig. 2a shows no cracks in deposits from 0.06M solution. This is thought to be because of the low Cr³⁺ concentration. All the other photographs show cracks, probably resulting from change of volume of the deposits because of chromium hydrides that are decomposed to chromium and hydrogen gas. Considering current efficiency and surface morphology of the deposits, the apparent optimal concentration of Cr³⁺ ranges from 0.2 to 0.4 M.

Effect of Hypophosphite Ions
Sodium hypophosphite was dissolved in aqueous solutions containing 0.073 M chromic chloride, 3.28 M ammonium chloride, 0.64 M boric acid, and 0.6 M sodium fluoride. The resulting solutions contained concentrations of sodium hypophosphite ranging from 0 to 3 M and were electrolyzed at an average cathodic current density of 0.15 A/cm² for six minutes at temperatures from 23 to 420°C. Test cell voltage varied from 7 to 10 volts.

No chromium deposits were obtained when the hypophosphite concentration was below 0.1 M, but were observed when concentration exceeded 0.2 M. Changes in pH were small, from 5.14 to 5.18, indicating that hypophosphite ions were acting as a buffer and thus were important in maintaining bath stability. Increasing the concentration of hypophosphite ions increases covering power and current efficiency, as shown in Fig. 3.

![Fig. 3—Effect of hypophosphite ion on current efficiency.](image)

The mechanism of the deposition of trivalent chromium has not been clear, but a possible explanation is that the Cr³⁺ is reduced to divalent chromium, then further reduced to chromium metal, with the divalent ion determining the rate of deposition. Hypophosphite is a reducing agent, so that the Cr²⁺ quickly obtains the necessary electron to

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become divalent. The trivalent ion can be oxidized to $\text{Cr}^{6+}$ at the anode, but the presence of the hypophosphite ion can hold this to a minimum.

Trivalent chromium plating baths include complexants such as carboxylic or thiocyanate ion, etc. The operating pH of the baths must be held between 2 and 4. Precipitation occurs if the pH is greater than 4, but baths containing hypophosphite can operate at pH greater than 5. Not only can hypophosphite ions stabilize trivalent chromium ions at higher pH, but chromium hydroxide precipitation is prevented at the cathode. The range of pH over which baths containing hypophosphite can operate is 2 to 5.5.

According to Espenson and Binua, the combination of trivalent chromium ions and hypophosphite ions can form chromium hypophosphite complex ions. The surface morphology of deposits at 0.2 to 4 M hypophosphite shown in Fig. 4a-f indicates nodular crystallinity, but with crack lines appearing in the deposits from the 0.6 and 2.3 M solutions. With the same considerations as before, the optimal concentration of hypophosphite ions appears to be 2.2 M.

![Fig. 4—SEM photographs of chromium deposits on brass cathodes in trivalent baths containing 0.1 to 4 M $\text{H}_2\text{PO}_2$.](image)

Figure 5 shows comparisons of X-ray diffraction patterns of deposits of trivalent chromium, hexavalent chromium and pure chromium metal. The trivalent chromium deposits have a peak (110) plane, while the hexavalent and pure chromium deposits show peaks (210) and (110) planes. The sharp peak in Fig. 5a and 5b is caused by the brass substrate. Another trivalent chromium deposit was identified by ESCA. It was found that there are two peaks of X-ray photoelectron spectra at 129.8 and 134 eV, corresponding to the binding energy of phosphorus. Therefore, the structure of trivalent chromium deposits is different from that of hexavalent chromium.

![Fig. 5—Comparison of X-ray diffraction patterns of chromium (a) deposit on brass cathode in trivalent bath; (b) deposit on brass cathode in hexavalent bath; (c) pure chromium.](image)

**Effect of Ammonium Ions**

Ammonium chloride was dissolved in aqueous solutions of 0.073 M chromic chloride, 2.2 M sodium hypophosphite, 0.6 M sodium fluoride, and 0.2 M boric acid. The resulting solutions contained concentrations of ammonium chloride ranging from 0 to 7.2 M and were electrolyzed at an average cathodic current density of 0.15 A/cm$^2$ for six minutes at temperatures from 19 to 59 ºC. Test cell voltage varied from 7 to 10 volts. No deposits were formed on the cathode at concentrations less than 0.4 M, but were observed when concentration was greater than 0.8 M. Increased concentration of ammonium ions increases throwing power and current efficiency, as shown in Fig. 6.

In these plating baths, both ammonium and chloride ions increase conductivity. Both form complex ions with $\text{Cr}^{3+}$. Why ammonium chloride can increase current efficiency is worthy of further investigation. The SEM photographs of the chromium deposits obtained are shown in Fig. 7. The deposits are amorphous for concentrations between 0.8 and 2.4 M. They are nodal crystal for concentrations...
Effect of Boric Acid

Boric acid was dissolved in aqueous solutions of 0.073 M chromic chloride, 2.2 M sodium hypophosphite, 0.6 M sodium fluoride, and 3.86 M ammonium chloride. The resulting solutions contained concentrations of boric acid ranging from 0.1 to 1.0 M and pH of 3.24 to 5.46. They were electrolyzed at an average cathodic current density of 0.15 A/cm$^2$ for three minutes at temperatures from 23 to 44 $^\circ$C. Test cell voltage varied from 7 to 12 volts. When boric acid is not contained in the plating solution, the deposit is shiny, but throwing power is small and pH changes are large, i.e., the baths are unstable. Increasing the concentration of boric acid results in stable pH because it is a good buffer. Without it, the pH at the boundary layer of deposits will increase and Cr(OH)$_3$ can be produced. The effect of the concentration of boric acid on current efficiency for trivalent chromium plating baths is shown in Fig. 8. Current efficiency is highest at low concentration, but becomes nearly constant, though lower, with increasing concentration.

The SEM photographs of Fig. 9 show the surface morphology of deposits obtained with varied concentrations of boric acid. At 0.1 M and below, the deposits are cracked, partly because of insufficient buffering and partly because of chromium hydrides decomposed to chromium and hydrogen. At 0.2 M, cracks are few, but there are also nodular deposits. At 0.6-0.8 M, the deposits are crack-free, not nodular, and close to amorphous in structure, with reduced hardness, demonstrating that the influence of boric acid on chromium deposits is significant. With the concentration of boric acid above 1.0 M, the deposits are held together by the buffer, showing the effect of boric acid on chromium deposits is significant.
Fig. 11 —Effect of current density on chromium current efficiency for trivalent baths containing 0.4 M Cr\(^{3+}\), 2.2 M NaH\(_2\)PO\(_2\), 3.28 M NH\(_4\)Cl, 0.2 M H\(_3\)BO\(_3\), and 0.1 M NaF.

Conclusions

The optimal trivalent chromium plating bath was established through investigation of composition and operating conditions of different solutions. The recommended formulation is as follows: 32 to 63 g/L of chromic chloride (CrCl\(_3\)), 194 g/L of sodium hypophosphite, 320 g/L of ammonium chloride, 12 g/L of boric acid, and 4 g/L of sodium fluoride. Operating conditions pH 2 to 5.5, 25 to 35°C, current density 0.02 to 0.5 A/cm\(^2\), maximum current efficiency 22 percent. Anodes graphite and platinized titanium. The color of the deposit is shiny white, richer and more attractive than that of hexavalent chromium deposits.

References

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